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FIRST ANNUAL TECHNICAL REPORT FOR INSTRUMENTATION GRANT

STATUS AND USE OF HPLC-DAD/APCI-MS AND DIRECT FLAME SAMPLING/APCI-MS FOR FULLERENES AND PAH RESEARCH

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DESCRIPTION OF INSTRUMENT:

The PE/Sciex APCI/LC-MS equipment consists of a high performance liquid chromatrograph (HPLC) with diode array spectrophotometric detector (DAD) interfaced to an atmospheric pressure ionizer with a single quadrupole mass spectrometer (MS)through a heated nebulizer. The interface between the HPLC and the MS is designed to minimize thermal input to the HPLC eluents and is of great importance for our intended application. Ionization occurs in a unique fashion at atmospheric pressure using a chemical ionization source (APCI). The equipment is being used for the identification and quantification of flame-generated fullerenes and polycyclic aromatic hydrocarbons (PAH).

The mode of operation of this instrument is as follows: (i) Complex mixtures are separated by the HPLC; (ii) UV spectra of separated components are obtained by the diode array detector (DAD) as they elute from the HPLC; (iii) components undergo mild ionization in the APCI source; and, (iv) mass spectra are acquired by the mass spectrometer.

STATUS AND USE OF THE EQUIPMENT:

The instrument if fully operating and has been very useful for the fullerenes project and several other projects as listed in Table 1. As can be seen in the table, the uses include not only fullerenes analyses but also studies of PAH metabolites, anticancer drugs, high MW PAH from flames, and products of wood combustion and napththalene pyrolysis. A considerable amount of time during the first year was spent dealing with various equipment problems and performing calibrations.

OPERATION AND MAINTENANCE:

The operation and maintenance of the equipment has been carried out by the Permanent Staff of the Core Laboratory in Analytical Chemistry, listed in Table 2, with service personnel from the company that made the equipment.

The Staff of the Permanent Core Laboratory are supported by MIT from research projects using the equipment. The services of personnel from the company are provided under a service

contract ($15,000/yr for the first year and $20,000/yr for the second year now beginning). The service contract is funded by research projects using the equipment.

NEW RESEARCH PROJECTS:

The following new research projects were undertaken as a result of the equipment being available: (1) study of giant fullerenes (C_n, n>100) in flames; (2) search for endohedral fullerenes in flames seeded with iron and cobalt; (3) search for C_{50}, a fullerene containing adjacent pentagons in its structure, in flames; (4) search for fullerenes in wood flames representative of forest fires and a potential natural fullerene source; (5) analysis of high molecular weight PAH soot precursors in flames; (6) stabilization of PAH and fullerene radicals by hydrogen-atom abstraction from molecular hydrogen; (7) synthesis of fullerenes by naphthalene pyrolysis; and (8) search for total resonance sextet PAH in o-terphenyl pyrolysis.

FACULTY AND STUDENTS WHO USED THE EQUIPMENT:

Six faculty members at MIT (Table 3) have used the equipment. Faculty members at other colleges and universities and researchers at the Naval Research Laboratory who have used the equipment are listed in Table 4. Ten graduate students and four undergraduates, listed in Table 5, have used the equipment.

RESULTS AND BREAKTHROUGHS:

Several important experimental results and breakthroughs achieved in using the equipment are summarized as follows: (1) giant fullerenes have been found in samples of condensable material collected from flames; (2) PAH compounds having molecular weights up to 2000 daltons were found to be present in methylene chloride extracts of soots from certain flames; (3) hyudrogen-gas injection into a probe collecting soot, PAH and fullerenes from flames was found to affect the mass spectrum of the compounds collected, consistent with radicals stabilization by the hydrogen; and (4) the synthesis of fullerenes by pyrolysis of naphthalene at 1000°C was confirmed, but also found to be highly sensitive to experimental conditions.

Table 1. APCI/LCMS Instrument Useage

INVESTIGATOR or PROJECT	PROJECT DESCRIPTION	RESULTS
1. S. Tannenbaum	PAH metabolites	structure identification
2. Dedon	Anticancer drug	structure confirmation
3. Naval Research Lab	fullerene oxidation samples	novel fullerene products
4. J. R. Degenfelder	Russian mineral fullerene source	C60 found in sample
5. wood combustion samples	Search for natural fullerenes	none detected
6. PFR ethylene flames	Analysis of high MW PAH & fullerenes	existing data confirmed
7. PFR naphthalene inj. flames	Analysis of high MW PAH & fullerenes	high MW PAH found
8. fullerene forming flames	Analysis of fullerene soots	large amounts data obtained
9. naphthalene pyrolysis	Drop-tube furnace study	high MW PAH found
10. o-terphenyl pyrolysis	Search for total resonance sextet PAH	TRS PAH discovered
11. Fullerenes from naphthalene	Pyrolysis of naphthalene > fullerenes	Trace amnts of C60 found
12. S. Tannenbaum	Nucleic acid modification	structure determination
13. K. C. Swallow	Photooxidation of PAH	Photoproduct structures
14. W.G. Thilly	Air toxics investigation	structure elucidation

CORE LAB STAFFING AND LCMS UTILIZATION

Table 2. Core Laboratory in Analytical Chemistry: Permanent Staff

name	position/title	dates employed	support
Dr. Arthur L. Lafleur	Principal Investigator	4/1/89 - present	100%
Dr. Koli Taghizadeh	Research Scientist	10/1/92 - present	100%
Elaine F. Plummer	Facilities Coordinator	4/1/89 - present	100%
John LoRusso	Instrumentation Specialist	10/1/93 - present	
John Durant	postdoctoral associate	3/94 - preseent	

Table 3. LCMS Research Participants at MIT

name	department	research program
A. F. Sarofim	Chemical Engineering	EPA Air Toxics Ressearch Center
J. P. Longwell	Chemical Engineering	Health Effects of Fuels Utilization
J. B. Howard	Chemical Engineering	Fullerenes Project, Air Toxics
P. Dedon	Toxicology	Center for Environ. Health Sciences Research Affiliate
H. Hemond	Civil and Envronmental Engineering	Superfund Hazardous Substances Basic Research Program
S. Tannenbaum	Toxicology	Superfund Hazardous Substances Basic Research Program

Table 4. LCMS Research Participants outside MIT

name	institution	research program
K. C. Swallow	Meriimack College	Photooxidation of PAH
G. Cass	California Institute of Technology, Chem. Eng.	EPA Exploratory Ressearch Center
M. J. Wornat	Princeton University	Pyrolysis of fuels products
Mark Ross & Steve McElvany	Naval Research Lab	Fullerenes structure elucidation

Table 5. Student Research Participants

(a) Doctoral Candidates

name	project designation		name	project designation
Joseph A. Marr	[A-Fuel-1]		Jaideep Mukherjee	[A-Fuel-2]
Jan Thijssen	[A-Fuel-3]		John Allen	[A-Fuel-2]
John Durant	[Superfund-B5]		Tapesh Yadav	[A-Fuel-1]
Mary J. Wornat	[A-Fuel-2]		Michael Masonjones	[Superfund-A13]
Bill Grieco	Fullerenes Project		Tim Benish	Fullerenes Project

(c) Undergraduate Students (UROP)

Laura Giovanne	[A-Fuel-1]		Susan Weakland	[A-Fuel-1]
Rose Marino	[A-Fuel-1]		Anna Chwang	[A-Fuel-1]

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9/16/94

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